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GREEN CONTAINER GLASS BASED ON FERROCHROMIUM INDUSTRIAL SLAG

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The possibility of using ferrochromium slag added into the material in the amount of more than 6% (up to 20%) is considered. The physicochemical properties of synthesized samples are investigated, their working parameters (temperature interval of forming, relative speed of the machine, crystallization index) are identified. The glass of this composition satisfies all requirements imposed on its working properties and can be recommended for the production of green glass bottles.

Waste generated by the metallurgical industry is now finding application in the glass industry along with traditional raw materials.

We have investigated the possibility and conditions of synthesizing glasses using recycled concentrated slag named "Larnite" (generated in production of low-carbon ferrochromium). The slag contains a large amount of modifier oxides (48.1% CaO and 13.4% MgO; here and elsewhere, wt.%), therefore, it was added to the glass batch to replace raw materials introducing CaO and MgO (particularly, to partly replace expensive ground dolomite), as well as Al_2O_3 and SiO_2. The batch for green glass was prepared using quartz sand, slag, soda, sulfate, and oxides of alkali-earth metals, varying the slag : dolomite ratio. The batch composition was corrected taking into account the slag additive. The chemical composition of glass in this case remained unchanged (%): 72.4 SiO_2, 2.5 Al_2O_3, 0.2 Fe_2O_3, 6.0 CaO, 3.9 MgO, and 15.0 Na_2O. Glass composition ZT-1 [1] was taken as the reference composition. The slag contains 5.95% Cr_2O_3, accordingly, no pigment for producing green color is introduced. Thus, the Larnite slag not only contributes the required oxides into glass, but also serves as a colorant, which is economically advantageous.

Glass was melted at a temperature of 1350 – 1400°C for 3.5 h, cast in preheated graphite molds, and annealed in a muffle furnace to remove residual stresses. The total duration of annealing was 1.5 h.

The obtained glasses had a dark green color with sufficient clarity (when 1/5 glass batch was replaced by slag, the sample were insufficiently clear). The melting, working, and service properties of glass were analyzed for their compliance with the main technological requirements imposed on container glasses with a view of forming on contemporary IS machines,

The viscosity of glass was determined by pressing an indenter. To reach a uniform indentation rate, the temperature was gradually increased. The dependence $\log \eta - 1/T$ was constructed (Fig. 1) and the graphic method was used to calculated the viscous flow activation energy that was equal to 387 kJ/mole.

According to Okhotin's method [2], characteristic temperatures accepted in container glass melting and working were determined for the set of viscosities:

– melting temperature: 1526°C corresponding to $\log \eta = 1$ (viscosity expressed in Pa · sec);

– drop temperature: 1223°C, $\log \eta = 2$;

– temperature of glass working or forming: 1041°C, $\log \eta = 3$;

– Littleton temperature t_S: 718°C, $\log \eta = 6.65$;

– fluidity temperature: 655°C, $\log \eta = 8$;

– temperature at which deformation is still possible: 623°C, $\log \eta = 9$;

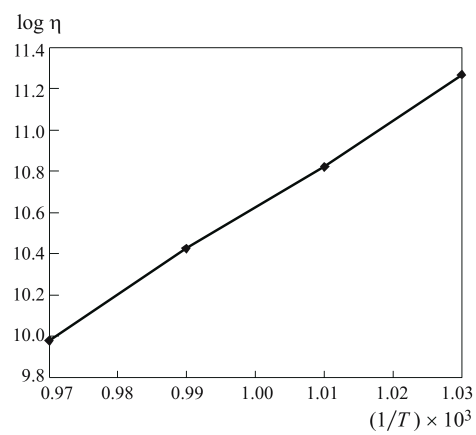

Fig. 1. Dependence of viscosity logarithm on inverse temperature.

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– softening temperature t_ω : 594°C, log η = 10;
– upper temperature of annealing t_A : 544°C, log η = 12;
– vitrification temperature t_g : 537°C, log η = 12.3;
– lower temperature of annealing: 513°C, log η = 13.5.

The estimated temperatures listed above made it possible to determine the working indexes for glass of a preset composition. The glass is regarded as suitable for forming on high-speed IS machines if its temperature interval of forming (TIF) is within the limits of 170 – 180°C:

$$\text{TIF} = t_S - t_A = 174.4°\text{C}.$$

The relative speed of a glass-forming machine (RSGM) is the working index of glass characterizing its efficiency. The recommended RSGM interval is in the limits of 104 – 110%:

$$\text{RSGM} = \frac{100(t_S - 450)}{(t_S - t_A) + 80} = 105.5\%.$$

The crystallization index (CI) is the working index of glass characterizing its propensity for crystallization. If the CI value is below zero, the glass is prone to crystallization (CI index has to have a positive value):

$$\text{CI} = (t_S - t_A) - 170 = 4.4°\text{C}.$$

Thus, the particular glass composition satisfies all requirements imposed on the working properties of container glass.

The thermal properties of glass have been studied as well, in particular, the thermal expansion of glass in the interval ranging from room temperature to glass softening temperature was determined using a vertical quartz dilatometer. The experimental CLTE valued was estimated as $87.3 \times 10^{-7}\ \text{K}^{-1}$ and the theoretical value (according to Appen's method) was calculated as $91.8 \times 10^{-7}\ \text{K}^{-1}$. The discrepancy between the experimental and theoretical values was about 5%. The thermal expansion curve (Fig. 2) was used to determine the characteristic temperatures: $t_g = 530°\text{C}$, $t_\omega = 600°\text{C}$.

The dilatometric temperatures correspond to the values calculated based on Okhotin's method.

The density of glass ρ was determined using the methods of Appen and Knapp [2].

The density of glass is:

by Appen's method:

$$\rho = \frac{\sum P_i}{\sum n_i \bar{V}_i} = 2.4803\ \text{g/cm}^3,$$

where $\sum P_i$ is the sum of the weight content of each components in glass, %; n_i is the number of moles of the ith component (weight content divided by molecular weight), molar parts; $\bar{V}_i$ is the approximated-averaged partial value (additive

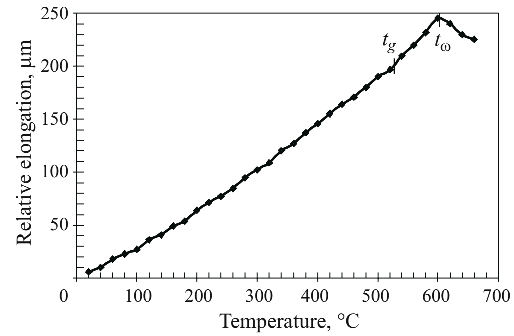

Fig. 2. Curve of thermal expansion of glass.

coefficient) of the specific volume of the respective component;

according to the Knapp's method:

$$\rho = P_1\rho_1 + P_2\rho_2 + P_3\rho_3 + \ldots + P_i\rho_i = 2.4803\ \text{g/cm}^3,$$

where P_1, P_2, P_3, ..., P_i are the weight contents of oxides in glass, %; ρ_1, ρ_2, ρ_3, ..., ρ_i are coefficients for density calculation.

As the density of container glass varies within the range of 2.2 – 2.5 g/cm^3 [3], the glass produced using Larnite slag satisfies the specified interval.

The refractive index of glass n was calculated by Appen's method [2]:

$$n_{D_{\text{SiO}_2}} = \frac{\sum \bar{n}_{D_{\text{SiO}_2}} n_i}{\sum n_i} = 1.5132,$$

where $\bar{n}_{D_{\text{SiO}_2}}$ is the approximated-averaged partial value of the refractive index for each component.

The elasticity modulus E and the sheer modulus G of glass were determined using Appen's method [2]:

$$E_{\text{SiO}_2} = \frac{\sum \bar{E}_{\text{SiO}_2} n_i}{\sum n_i} = 7020.6\ \text{kgf/mm}^2 = 68{,}801.9\ \text{MPa};$$

$$G_{\text{SiO}_2} = \frac{\sum \bar{G}_{\text{SiO}_2} n_i}{\sum n_i} = 2840.8\ \text{kgf/mm}^2 = 27{,}839.8\ \text{MPa},$$

where $\bar{E}_{\text{SiO}_2}$ and $\bar{G}_{\text{SiO}_2}$ are the approximated-averaged partial values of elasticity modulus and sheer modulus for each component.

The elasticity modulus for soda-lime glasses ranges from 48,000 to 83,000 MPa and the shear modulus from 22,000 to 28,000 MPa [1]. The calculated values are within the prescribed limits, therefor, satisfy the requirements.

The heat capacity of glass C_{gl} was calculated using Sharp and Guintner's method [2], who proposed a formula for determining heat capacity in a wide temperature interval (from

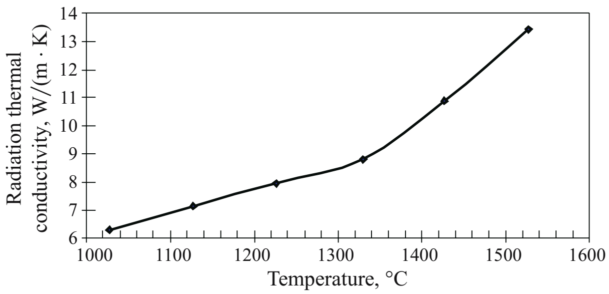

Fig. 3. Radiation thermal conductivity of green glass depending on temperature.

– 200 to + 1300°C) for the working temperature of glass (t_{gl} = 1280°C):

$$C_{gl} = \frac{1}{0.00146 t_{gl} + 1}[p_1(a_1 t_{gl} + C_1) + p_2(a_2 t_{gl} + C_2) + \ldots + p_i(a_i t_{gl} + C_i)] = 0.2931\ \text{kcal}/(\text{kg} \cdot \text{K}) = 1.23\ \text{kJ}/(\text{kg} \cdot \text{K}),$$

where $p_1, p_2, \ldots, p_i$ are the contents of individual oxides in glass, weight parts and $a_1, a_2, \ldots, a_i$; $C_1, C_2, \ldots, C_i$ are calculation coefficients.

The thermal conductivity of glass λ_{gl} was determined based on Wilner's and I'lina's coefficients providing not more than ± 5% deviation from experimental results [2]:

$$\lambda_{gl} = \lambda_1 p_1 + \lambda_2 p_2 + \ldots + \lambda_i p_i = 0.97\ \text{W}/(\text{m} \cdot \text{K}),$$

where $\lambda_1, \lambda_2, \ldots, \lambda_i$ are additive coefficients for calculating thermal conductivity of glass.

The calculated thermal conductivity value agrees with reference data for green glass [4].

The radiation thermal conductivity of green glass has been calculated [2]:

$$\lambda_{rad} = 30 - 47.5 \times 10^{-3} t + 23.93 \times 10^{-6} t^2 = 8.69\ \text{W}/(\text{m} \cdot \text{K}),$$

where t is the temperatures of the surface of green glass equal to 1300°C.

The dependence of radiation thermal conductivity on temperature is given in Fig. 3.

The chemical resistance of glass has been analyzed [4], which depends on its chemical composition and the type of reactants. The determination of water resistance at 98°C established that the particular green glass is resistant (III hydrolytic class).

Thus, the experiments and theoretical calculations prove the possibility of synthesizing glasses using ferrochromium slag. The analysis of the physicochemical and working properties of obtained glass makes it possible to recommend the specified slag as a glass batch component for producing green glass bottles.

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